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(54) **Carbonless system including solvent-only microcapsules.**

(57) A carbonless system having improved imaging characteristics by the use of microcapsules containing only solvent is disclosed. The solvent-only capsules are disposed within a carbonless system to enhance the resulting image without the use of additional dye precursor.

CARBONLESS SYSTEM INCLUDING SOLVENT-ONLY MICROCAPSULES

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to carbonless copying
5 systems.

Description of the Prior Art

Carbonless copying systems usually include a plurality
of paper sheets or substrates arranged in a manifold set,
each sheet of the set having one or more coatings on its
10 surfaces. The manifold set is designed so that when a
marking pressure caused by a typewriter, pen, or other
instrument is applied to the outermost sheet, a colored mark
will be formed on at least one surface of each sheet of the
manifold set.

15 To this end, the top sheet of the manifold set to which
the marking pressure is applied is provided with a coating
on its back surface. This coated back surface includes
microcapsules containing an initially colorless chemically
reactive color-forming dye precursor as the fill material.
20 The upper surface of the next sheet, which is adjacent to
the back surface of the top sheet, is coated with a material
containing a component, such as phenolic resin or reactive
clay, that is capable of reacting with the colorless dye
precursor contained in the microcapsules to produce a color.
25 Thus, a marking pressure on the upper surface of the top
sheet will rupture the microcapsules on the bottom surface
and release the colorless dye precursor. The colorless dye
precursor then chemically reacts with the reactive component
of the coated front of the lower sheet to produce a colored
30 mark corresponding to the area of marking pressure. In
similar fashion, colored marks are produced on each succeeding
sheet of the manifold set by the marking pressure rupturing
the microcapsules carried on the lower surfaces of each sheet.

The sheets of the manifold set in carbonless copying

systems are designated in the art by the terms CB, CFB, and CF, which stand respectively for "coated back", "coated front and back", and "coated front". The CB or transfer sheet is usually the top sheet of the manifold set and the
5 sheet upon which the marking pressure is applied. The CFB sheets are the intermediate sheets of the manifold set, each of which is able to have a mark formed on its front surface by a marking pressure and each of which also transmits the contents of ruptured microcapsules from its back surface
10 to the front surface of the next sheet. The CF or recording sheet is the bottom sheet and is only coated on its front surface so that an image may be formed on it.

While it is customary to have the coating containing the microcapsules on the back surface of the sheets and to
15 have the coating containing the reactive component for the capsules on the front surface of each of the sheets, a reverse arrangement is also possible. In addition, one of the reactive ingredients may be carried in the sheets themselves, rather than applied as surface coatings. Furthermore,
20 the reactive component for the colorless dye precursor may be microencapsulated instead of or in addition to the precursor. Patents illustrative of the various kinds of systems that may be used in the production of manifold carbonless copying systems include by way of example: US Patent Nos. 2,299,694
25 (Green); 2,712,507 (Green); 3,016,308 (Macaulay); 3,429,827 (Ruus); and 3,720,534 (Macaulay et al.).

The microcapsules used in carbonless systems generally comprise a core of fill material surrounded by a wall or shell of polymeric material. The wall surrounding the fill material
30 acts to isolate the fill material from the external environment. When it is desirable to release the fill material, e.g. the dye precursor, the capsule wall may be ruptured by mechanical pressure, for example, thereby introducing the fill material into its surroundings. Generally, microcapsules
35 comprise separate and discrete capsules having non-interconnecting hollow spaces. The fill material is thus enveloped within the generally continuous polymeric walls of the microcapsules, which may range from 0.1 to approximately

500 microns in diameter.

In carbonless systems it is desirable to obtain a strong image on the recording or CF sheet. One way of enhancing the image of a carbonless system is to increase the concentration of the dye precursor contained in the microcapsules coated on the CB sheet. However, this method of image enhancement suffers from a serious drawback in that dye precursors are generally quite expensive. Therefore, any increase in the concentration of dye precursor in the CB microcapsules necessarily increases the cost of the carbonless copy system. A second solution is to coat more dye containing microcapsules on the transfer or CB sheet. This, however, suffers from the same drawback as the first proposed solution since a greater amount of expensive dye precursor is used in the resulting carbonless system. Thus, there is a need for a carbonless copy system that produces an enhanced image without using an economically prohibitive amount of expensive dye precursor.

Microcapsules that contain only an organic solvent for use in carbonless copy systems are disclosed in U.S. Patent Nos. 3,663,256 (Miller et al.) and 3,672,935 (Miller et al.). Both of these patents disclose at Figure 2 (I, Ia, Vb, Vc, and Vd) the use of solvent-only capsules coated on the CB sheet of a manifold system or in a self-contained carbonless system. In each of these schematic diagrams neither of the two reactive mark forming components, i.e. the dye precursor and the clay, is microencapsulated. Thus, the solvent-only microcapsules shown in the Miller et al. patents are the only sources of solvent in these proposed carbonless systems.

The Miller et al. carbonless systems disclosed at Figure 2 (I, Ia, Vb, Vc, and Vd) have not met with widespread commercial acceptance. Since microencapsulation is the surest means of isolating the mark forming components from each other prior to pressure imaging, the above systems increase the likelihood of inadvertent color development that is a common problem in carbonless copy systems. Premature discoloration has been variously

referred to as blush, offset, bluing, ghosting, and backprint. Whatever it is called, it is highly objectionable and undesirable in a carbonless copying system.

The following patent documents disclose various architectures known in the carbonless copying art: U.S. Patents Nos. Re. 30,041 (Maalouf); Re. 30,116 (Maalouf); 4,003,589 (Konishi et al.); 4,071,469 (Vincent et al.); 4,096,314 (Cespon); 4,130,299 (Wygant); 4,147,830 (Kato et al.); 4,187,233 (Petitpierre); 4,211,436 (Kuhlthau et al.); 4,250,098 (Chang); 4,287,074 (Earhart et al.); 4,295,662 (Tutty); 4,309,047 (Petitpierre); 4,316,036 (Petitpierre); 4,343,939 (Cesark et al.); 4,343,944 (Burri); 4,355,823 (Burri); 4,363,503 (Schmidt et al.); and 4,372,581 (Schumacher et al.); and United Kingdom Patent Specifications Nos. 1,290,369 (Fuji); and 1,417,206 (Mizusawa). None of the patents listed above discloses the use of microcapsules that encapsulate a fill material consisting solely of solvent.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide an improved carbonless copying system. It is a further object of the present invention to provide a carbonless copy system having enhanced imaging capability without increased usage of dye precursor.

According to the present invention there is provided a carbonless copying system including two types of microcapsules. The first type of microcapsule encapsulates either a solution or suspension containing one of the two mark forming components of the carbonless system. Thus, the first type of microcapsule contains either the dye precursor or the reactive clay or resin in solution or suspension. The second type of microcapsule encapsulates only solvent, the solvent being capable of dissolving or suspending either or both of the mark forming components. Thus, the second type of microcapsule does not contain any dye precursor or reactive clay or resin. By contrast, the fill material encapsulated within the second type of

microcapsule consists only of solvent, either a single solvent or a mixture of solvents. The two types of microcapsules and the second mark forming component are then arranged in juxtaposed pressure-sensitive contact with respect to one another such that when marking pressure is applied to the carbonless system, both types of microcapsules rupture releasing the solvent contained in the second type of microcapsule and the solution or suspension contained in the first type of microcapsule. The first marking component and the second marking component are thus brought into reactive contact and form an image. The presence of the solvent-only microcapsules, however, improves the intensity of the resulting image.

Preferably, the solvent-only microcapsules are coated on the CF along with unencapsulated reactive clay or resin. The CF is then reacted with a conventional CB sheet to form an enhanced image without the need of additional dye precursor. While the solvent-only capsules are desirably coated on the CF or recording sheet, the presence of such capsules in the CB or transfer sheet coating or in both the CF and CB coatings may also result in improved imaging in certain carbonless systems. In addition, the present invention has utility in self-contained carbonless systems.

25 DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the present invention, microcapsules encapsulating a fill material consisting solely of a solvent that is capable of dissolving either or both of the mark forming components is added to any of a variety of conventional carbonless copying systems. The solvent-only capsules may be incorporated in the CF coating, the CB coating, or both. Additionally, the solvent-only capsules may be used in the context of a self-contained carbonless copy system. Though incorporation of the solvent-only capsules in the CF coating is preferably advantageous with respect to the enhancement of the resulting image, the presence of the

solvent only capsules at any point where they are in reactive contact with the two mark forming components may result in image enhancement in certain carbonless systems.

The microcapsules encapsulating only solvent should
5 contain a solvent that is capable of dissolving or suspending either the dye precursor or the reactive clay or phenolic resin or both. Suitable solvents include such organic solvents as benzyl butyl phthalate, dibutyl phthalate, toluene, various xylenes, alkyl benzenes, alkyl naphthalenes,
10 diaryl methanes, diaryl ethanes, and alkyl biphenyls or mixtures thereof.

In a preferred embodiment, the fill material to be encapsulated within the first type of microcapsule will usually be a colorless dye precursor such as Crystal Violet
15 Lactone, benzoyl leucomethylene blue, rhodamine lactam, the p-toluene sulfinic acid of Michler's hydrol, or any of the various chromogenic compounds that are capable of changing from a colorless to a colored form on contact with acidic substances, such as phenolic resins or reactive clays.

20 The present invention may be used with any of the known classes of microcapsules including polyamide, polyurea, polyurethane, polyester, urea-formaldehyde, melamine-formaldehyde, and gum arabic/gelatin.

Examples 1-9

25 Nine recording or CF sheets were prepared using resin CF formulations additionally containing various percentages of solvent-only capsules. Each of these nine CF formulations contained 85 parts of Astribrite, a high brightness kaolin coating clay made by Georgia Kaolin, 15 parts of Schenectady
30 HRJ-2162 resin, a zinc chelated para-alkyl substituted novalac phenolic resin manufactured by Schenectady Chemical Company, 10 parts of Starch P.G.290, produced by Penick and Ford, and 5 parts of Latex Dow 62Q, an SBR rubber produced by Dow Chemical Company. The CF formulations were coated
35 onto conventional bond at 6.4-7.1 gsm and the sheets of Example 2 only were supercalendered. The solvent encapsulated in the solvent-only microcapsules of Examples 3-5 and 7-9 was KMC 113 oil, which is a blend of diisopropyl naphthalenes

produced by Kureha Chemical Co. The CF sheets were then imaged against a black imaging CB suitable for producing images on a phenolic resin based CF. The reflectance values of the resulting images were recorded at three time intervals: (a) immediately after striking the surface of the carbonless system with a typewriter, (b) twenty minutes after impact, and (c) twenty-four hours after the initial strike. The solvent in the solvent-only microcapsules of Example 6 consisted of 50% by weight Santosol 150, a phenyl xylyl methane produced by Monsanto, and 50% by weight of Uthane-12, which is a C₁₀-C₁₅ linear alkyl substituted benzene produced by Union Carbide. The reflectance measurements were taken on a B & L Opacimeter. The lower the reflectance number, the better or more intense the image. The reflectance values based on percent by weight of solvent-only capsules in the CF coating are shown below for Examples 1-9.

		<u>Example</u>								
		1	2	3	4	5	6	7	8	9
20	Percent by weight of solvent-only capsules	0	0	1	3	5	5	8	10	15
25	Reflectance on impact	72.9	70.3	68.1	66.4	63.3	61.8	59.0	62.4	62.0
	after 20 min.	54.7	55.9	51.7	51.6	49.3	49.3	44.0	45.2	44.0
	after 24 hr.	52.5	53.2	49.1	49.1	46.7	46.7	41.8	42.4	41.8

Examples 10-18

Additional CF formulations were prepared using varying percentages of solvent-only microcapsules in a manner analogous to Examples 1-9. In Examples 10-18, each of the CF formulations contained 1.75 parts Dispex N-40, a sodium substituted polyacrylate made by Allied Corporation, 60 parts Siltan No. 6 clay, which is produced by Mizusawa Company, 40 parts Astribite, 5 parts Starch P.G. 290, and 15 parts Latex Dow 620. These CF formulations were coated on conventional

bond substrates at 6.4-7.1 gsm and the CF sheet of Example 11 was supercalendered. The resulting CF sheets were imaged against several types of black imaging CB's suitable for producing images on an acid-activated clay based CF. The reflectance values were measured on a B & L Opacimeter upon impact, after twenty minutes, and after twenty-four hours. The solvent used in the solvent-only capsules in Examples 12-14 and 16-18 was KMC 113 oil while the solvent used in Example 15 was a 50%-50% by weight mixture of Santosol-150 and Uthane-12. The results for the CF coatings based on percent by weight of solvent-only capsules in the CF coating are shown below.

Example

		10	11	12	13	14	15	16	17	18
15	Percent by weight of solvent-only capsules	0	0	1	3	5	5	8	10	15
20	<u>CB No.1</u> <u>Reflectance</u> on impact 20 min. 24 hr.	56.3 50.5 47.8	60.9 55.1 51.9	56.3 49.8 48.2	57.7 51.4 49.8	56.4 49.4 48.3	54.4 48.6 47.4	53.8 47.6 45.7	52.0 45.9 45.3	53.3 46.3 45.6
25	<u>CB No.2</u> <u>Reflectance</u> on impact 20 min. 24 hr.	55.2 48.2 43.3	60.0 52.8 47.3	55.0 46.5 43.3	54.9 46.8 43.5	53.7 45.4 42.3	51.4 43.4 40.8	50.7 42.8 39.5	50.1 41.7 39.0	50.4 41.6 39.2

Examples 19-21

30 In Examples 19-21, 15 parts of Durez 31623 resin, which is a zinc chelated octyl phenol resin produced by Occidental Corporation, was substituted for the 15 parts of Schenectady HRJ-2162 resin in the CF formulations of Examples 1-9. Example 21 used KMC 113 oil as the solvent in the solvent-only microcapsules. The resulting CF formulations were coated on ordinary bond paper and the CF sheet of Example 20 was supercalendered. The reflectance values for the resulting CF sheets when imaged against the three component black CB

are shown below:

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<u>Example</u>		19	20	21
5	Percent by weight solvent-only capsules	0	0	5
10	<u>Reflectance</u>			
	on impact	63.8	66.7	60.3
	20 min.	54.6	56.2	45.0
	24 hr.	53.3	54.8	43.7

As can be seen from Example 3, the addition of as little as one percent by weight of solvent-only capsules to a conventional CF formulation results in a significant increase in the intensity of the resulting image. The image enhancement continues to increase with the addition of higher percentage of solvent-only capsules with maximum image enhancement occurring somewhere between eight and ten percent by weight. Thus, the use of solvent-only capsules in a conventional CF formulation increases the image formed by the carbonless copy system without the necessity of increasing the use of expensive dye precursor. This results in a more desirable carbonless copy system and avoids the need to increase the use of costly precursors.

Examples 22-31

In the following examples, solvent-only microcapsules were added to a conventional black imaging CB formulation for carbonless copy systems. The solvent used in the dye precursor microcapsules was a blend of KMC 113 and Ucan 12. The solvent used in the solvent-only microcapsules consisted of a similar blend. The dye precursor microcapsules and the solvent-only microcapsules were coated at 2.8 gsm on conventional bond paper. Examples 22-26 used microcapsules containing a solution of chromogens that produced a suitable black image on phenolic resin based CF's. Examples 27-31 used microcapsules containing a solution of chromogens that produced a suitable black image on acid-activated clay based CF's. The various CB formulations were then imaged against appropriate CF's and the

reflectance values again recorded on a B & L Opacimeter immediately upon impact, after 20 minutes and after 24 hours. The results, based on the percentage of solvent-only microcapsules by weight in the CB coating, are shown below, including comparisons to similar image producing CB coatings having no solvent-only capsules with coating weights equivalent to the dye precursor microcapsule content in the coatings containing solvent-only capsules:

		<u>Example</u>									
10		22		23		24		25		26	
	Percent by weight of solvent-only capsules	0%	*	10%	*	20%	*	30%	*	40%	*
15	Coating weight of CB coatings (gsm)	2.80	2.80	2.80	2.52	2.80	2.24	2.80	1.96	2.80	1.68
20	<u>Reflectance</u>										
	On impact	58.4	58.4	58.2	59.6	59.0	60.9	59.1	62.1	61.3	63.3
	After 20 min.	38.3	38.3	38.4	40.7	40.6	43.0	42.1	45.4	45.6	47.8
	After 24 hrs.	35.4	35.4	36.4	37.5	38.3	39.6	40.1	41.7	44.1	43.8

		<u>Example</u>									
		27		28		29		30		31	
25	Percent by weight of solvent-only capsules	0%	*	10%	*	20%	*	30%	*	40%	*
30	Coating weight of CB coatings	2.80	2.80	2.80	2.52	2.80	2.24	2.80	1.96	2.80	1.68
<u>Reflectance</u>											
	On impact	44.0	44.0	44.4	46.3	46.7	48.6	48.2	50.9	54.2	53.2
	After 20 min.	38.7	38.7	39.6	41.0	41.1	43.4	42.4	45.7	49.5	48.1
	After 24 hrs.	35.7	35.7	35.2	37.4	38.2	39.1	39.2	40.8	44.5	42.5

35 * Same dye precursor capsule content, but no solvent-only capsules.

As can be seen from the results in Examples 22-31, the addition of solvent-only microcapsules to the CB coatings for carbonless systems generally results in increased image
40 intensity compared to similar CB coating containing no

solvent-only capsules. Theoretically, a wide latitude exists for incorporating large amounts of solvent-only capsules to the CB coating. However, at the higher percentages, intensity of the image compared to the
5 starting intensity deteriorates markedly due to dilution. For a given CB coating weight the optimum proportion of solvent-only microcapsules will be reached when the image intensity of the blended coating equals the image intensity of a coating identical in weight but with no solvent-only
10 capsules present. In the case of the above examples, this occurs when the level of solvent-only capsules is equivalent to 10-20% of the coating weight of the system.

The use of solvent-only capsules in a conventional CB formulation increases the image formed by the system without
15 the necessity of increasing the use of expensive dye precursor. This results in a more desirable carbonless copy system and avoids the need to increase the use of costly precursors. It is believed by applicant that the salutary results of the present invention are due to the
20 solvent in the solvent-only capsules aiding the penetration of the dye precursor into the reactive CF coating, whether clay or resin. However, applicant's invention is not to be limited by this hypothesis of the mechanism behind the advantageous results of the present invention. In addition,
25 it is to be understood that the above specification emphasizes certain embodiments and features of the present invention and that many other embodiments not specifically described may come within the spirit and scope of the present invention as hereafter claimed.

CLAIMS

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1. A carbonless copying system having a recording substrate, first and second mark-forming components capable of reacting with each other to produce a colored reaction
5 product, and a first type of microcapsule having generally continuous walls encapsulating a first fill material, the first fill material comprising a solution or suspension containing the first mark-forming component, characterised in that there is provided
10 a second type of microcapsule having generally continuous walls encapsulating a second fill material, the second fill material consisting of solvent capable of dissolving either the first or the second mark-forming component or both wherein the first and the second type of microcapsule and
15 the second mark-forming component being arranged in juxtaposed pressure-sensitive contact with respect to one another such that the application of marking pressure upon the carbonless system causes a colored mark to form on the recording substrate.
- 20 2. The carbonless copying system as claimed in Claim 1 characterised in that the first mark-forming component is a colorless dye precursor and the second mark-forming component is an acidic clay or phenolic resin.
- 25 3. The carbonless copying system as claimed in Claim 1 or 2 characterised in that the second fill material is an organic solvent capable of dissolving the colorless dye precursor.
- 30 4. The carbonless copying system as claimed in Claim 1, 2 or 3 characterised in that the second type of microcapsule and the second mark forming component are coated over at least a portion of the recording substrate.
- 35 5. The carbonless copying system as claimed in any one of the preceding Claims which additionally comprises a transfer substrate wherein the first type of microcapsule is coated over at least a portion of the transfer substrate.

6. The carbonless copying system as claimed in any one of Claims 1 to 3 which additionally comprises a transfer substrate wherein the second type of microcapsule and the first type of microcapsule are both coated over at least
5 a portion of the transfer substrate.